

# PATENT ABSTRACTS OF JAPAN

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(71)Applicant : TAKAMI TOMOHIDE  
INO SHOZO

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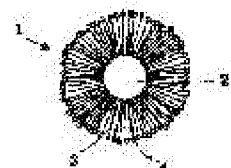
(72)Inventor : TAKAMI TOMOHIDE  
INO SHOZO

## (54) MICELLE TYPE METAL FINE PARTICLE AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain fine particles capable of using metal fine particles, which have been limited in use method and field hitherto, in various fields by absorbing molecular chain of an organic substance onto the surface of metal fine particles, and covering metal fine particles in micelle state.

SOLUTION: Micelle type metal fine particles 1 absorbing molecular chain 3 of organic substance having affinity for metal surface on the surface of multiple twin crystal particles 2 having 1-200nm particle diameter exhibit properties based on the terminal functional group 4 of a molecular chain 3. As the metal fine particles, various kinds of metal fine particles such as chromium, ZnTe, selenium, aluminum and copper can be used and especially, twin crystal particles of gold, silver, nickel, palladium, platinum, etc., are preferable. An alkanethiol such as mercaptoacetic acid or  $\beta$ -mercaptopropionic acid is used as the molecular chain 3 of the organic substance and carbon number of the alkyl chain is 2-18. Micelle type metal fine particles soluble in water are obtained by using a hydrophilic group such as hydroxyl group, carboxyl group, methyl group or phenyl group as the terminal functional group 4 of the molecular chain 3. Multiple twin crystal particles 2 are obtained by vacuum deposition onto substrate surface.



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## CLAIMS

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[Claim(s)]

[Claim 1]Micell type metal particles a chain of an organic matter having stuck to the surface of metal particles, and covering metal particles in the shape of micell in micell type metal particles.

[Claim 2]The micell type metal particle according to claim 1, wherein metal particles are multiplex twin crystal particles.

[Claim 3]A manufacturing method of micell type metal particles mixing multiplex twin crystal particles produced with vacuum deposition to a substrate face in a manufacturing method of micell type metal particles in a solution of an organic matter which has an adsorption group to a surface of metal.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a micell type metal particle having the character of the metal which the organic matter combined with minute metallic crystal particles, and an organic matter, and a manufacturing method for the same.

[0002]

[Description of the Prior Art]Metal particles are used in various fields. For example, covering metal particles with polyimide, or covering iron impalpable powder with an organic substance, and making a magnetic fluid is performed for many years. On the other hand, it is known that particles will reveal the unique character which is not revealed by big particles if the size of particles becomes small.

[0003]For example, research of the characteristic which the detailed substance of a nano order which is represented by  $C_{60}$  has, and research which uses those particles further are advanced. In the research process about the vacuum evaporation film of the gold formed in the alkali halide crystal surface, this invention person has discovered the multiplex twin crystal particles which the atomic number of gold of right decahedron and regular-icosahedron structure becomes from about 50-100 pieces. This particle has the structure which piled up the twin crystal of the shape of a regular tetrahedron which consists of {111} sides one after another.

They are the particles which have a unique structure and character of close packed structure.

[0004]

[Problem(s) to be Solved by the Invention]This invention makes it a technical problem to provide conventionally a particle which made usable the metal particles to which directions for use or a field was restricted in various kinds of fields, and a manufacturing method for the same.

[0005]

[Means for Solving the Problem]This inventions are the micell type metal particles which a chain of an organic matter stuck to the surface of metal particles, and covered metal particles

to a micell type in micell type metal particles. Metal particles are the aforementioned micell type metal particles which are multiplex twin crystal particles. A manufacturing method of micell type metal particles which mix multiplex twin crystal particles produced with vacuum deposition to a substrate face in a manufacturing method of micell type metal particles in a solution of an organic matter which has an adsorption group to a surface of metal.

[0006]

[Embodiment of the Invention]Namely, the micell type metal particles containing the metal particles of this invention, Like the micell which the chain of the organic matter joined together, and the chain of the surface-active agent carried out the hydrophilic radical outside the center [ a hydrophobic radical ] in underwater exactly, and gathered in the surface of metal particles spherically, They are the micell type particles which the chain of many organic matters stuck to the metal particle surface chemically, and were spherically formed in it. And the obtained micell type particles show various kinds of characteristics based on the chemical nature of the chain of the organic matter which stuck to the surface of metal particles or metal particles.

[0007]For example, by changing the end of the chain of an organic matter into various kinds of things like a methyl group, a hydroxyl group, and a carboxyl group, Adjust character including the solubility over inorganic substances, such as various organic matters and water, etc., or, Can produce the substance which has various functions, can produce the metal dissolved or distributed to water or an organic solvent, and as use art of metal including metaled spreading, By using physical characteristics including the unique optical physical properties which metal particles have, it is also applicable also as conversion material of an electron device or light energy.

[0008]As shown in drawing 1, the chain 3 of the organic matter which has a surface of metal and compatibility on the surface of metal particles, especially the multiplex twin crystal particles 2 is sticking to the micell type metal particles 1 of this invention, and micell type particles show the character based on the end functional group 4 of a chain.

[0009]Although various kinds of metal, such as chromium, ZnTe, selenium, aluminum, and copper, can be used as metal particles, multiplex twin crystal particles, such as gold, silver, nickel, palladium, platinum, iron, cobalt, and indium, are especially preferred. As for the particle diameter of metal particles, it is preferred that they are 1 nm - 200 nm, and it is more preferred that they are 10 nm - 100 nm. Since micell mold structure will not be formed if smaller than 1 nm, it is not desirable, and since it stops having the specific character as particles when larger than 200 nm, it is not desirable.

[0010]As a chain of an organic matter, alkane thiols, such as mercaptoacetic acid, beta-mercaptopropionic acid, and dodecanethiol, etc. are preferred, and the carbon number of an alkyl chain has a preferred thing of 2-18. As for a chain, what seldom causes steric exclusion by linear shape is good, and since obstacles, like a chain bends will be encountered if a carbon number becomes 20 or more, it is not preferred. More than  $10^{-7}$  mol/l of the concentration of an organic matter is preferred, and an organic matter required if it becomes less than it, in order to form micell mold structure becomes less insufficient. as an end functional group of the chain of an organic matter, a hydroxyl group, a carboxyl group, a methyl

group, a phenyl group, etc. are mentioned -- things can be carried out. The micell type particles dissolved to water are producible by using a hydrophilic radical as an end functional group. The substance etc. which have an adhesive property to metal, such as 4-META (4-metacryloxyethyl trimellitate anhydride), can be used. Micell type particles are producible by mixing metal particles in the solution containing the chain of the organic matter made to stick to metal particles.

[0011]An example of the manufacturing process of the micell type metal particles of this invention is explained with reference to drawing 2. Drawing 2 is a figure explained by a section. As shown in drawing 2 (A), into a vacuum, on the surface of the alkali halide crystals 5, such as salt, a metaled atom is vapor-deposited by a thickness of tens of nm, and the metal particles 6 are formed. As for the degree of vacuum in vacuum deposition, it is preferred that below  $10^{-6}$  torr carries out. Subsequently, as shown in drawing 2 (B), the particles which vapor-deposited 100-200 nm of alkali halide, and produced it are thoroughly covered with alkali halide. As shown in drawing 2 (C), metal particles are further vapor-deposited on an alkali halide crystal face. By repeating the above process, as shown in drawing 2 (D), many metal particles 6 are producible. Metaled particles are not obtained, when the particles of the metal which adjoins in the case of metaled vacuum deposition unite and it becomes film-like metal. When metal arises in the shape of a film, it can check by the difference of a color from the metal of particle state. For example, in manufacturing golden particles by vacuum evaporation, it assumes a red purple color - blue by golden particles, but when gold foil arises, since it becomes golden, it can know that metal particles are not generating. Subsequently, the alkali halide which contained metaled particles as shown in drawing 2 (E), By dissolving into the solution 7 of the organic matter containing the chain to which it should stick, the chain of an organic matter sticks to the surface of the metal particles separated by the dissolution of alkali halide, and the micell type particles 1 of this invention as shown in drawing 2 (F) generate. Micell type particles can be separated from a solution and can be refined by the isolation column etc. which consist of polyimide etc. It is also possible to carry out separation refinement to residual substances, such as alkali halide and a thiol, by dialysis. It is meltable not only to alkali halide but a solvent, and a substrate is not combined with the metal used for metal particles, and if it forms with vacuum deposition, various kinds of substances can be used.

[0012]The solution containing the chain of the organic matter which sticks to the surface of metal particles, The solution of  $10^{-3}$  -  $10^{-6}$  mol/l has preferred concentration, when it is solution of mercaptoacetic acid and beta-mercaptopropionic acid, solution is preferred, and when it is a dodecane alkane thiol, the mixed liquor of ethanol and water is preferred. Since glycerin dissolves both alkali halide and an organic matter, when combining with the surface of metal particles the chain of the organic matter which does not dissolve in water, it can be used as a solvent.

[0013]Since the micell type metal particles of this invention are adsorbing the chain of a large number which become a surface of metal from an organic matter with an end functional group, they can reveal unique character, and they can use it for a metal particle material, the charge

of a metal finishing material, particle gel material, a metal \*\*\*\* thin film manufacturing device, a light energy inverter, etc.

[0014]

[Example]An example is given to below and this invention is explained to it.

Salt was vapor-deposited for the inside of example 1 vacuum devices in thickness of 100 nm on the 10 cm long and 10 cm wide substrate of ordinary temperature as a degree of vacuum of  $2 \times 10^{-6}$  torr. Subsequently, the temperature of the substrate was heated at 300 \*\*, the golden metal atom was vapor-deposited in thickness of 5 nm, and the particle with a particle diameter of 10-60 nm was produced. The transmission type microphotograph of metal particles is shown in drawing 3. The particles which have regular-icosahedron structure are shown. Furthermore, the temperature of the substrate was held at 300 \*\*, and salt was vapor-deposited in thickness of 100 nm. It carried out by having repeated the operation which vapor-deposits a golden metal atom in thickness of 5 nm, and vapor-deposits salt further on the formed salt, and the vacuum evaporation thing which contained in salt the metal particles which have ten layers of metal particle layers was obtained. The obtained vacuum evaporation thing was dissolved in the solution containing beta-mercaptopropionic acid of concentration  $10^{-3}$  mol/l, and the isolation column which consists of polyimide refined.

[0015]The obtained micell type metal particles are observed with the scanning electron microscope for ultrahigh vacuums (made by JEOL), and the result is shown in drawing 4. It is shown that micell is sticking to the metal particle surface shown in drawing 3.

[0016]The spectrum of the X-rays generated when the sample which applied the obtained micell type metal particles to the silicon surface is irradiated with the electron beam of 15keV is measured with X-ray spectrometer (Horiba make M-915), and the result is shown in drawing 5. Golden Malpha based on the Kinbara child, a beta ray, Lalpha, a beta ray, and K alpha rays based on the sulfur atom of an alkane thiol were observed. Based on the substrate to which Si made nano micell stick in drawing 5, Cl measures Cr and Fe based on the salt used at the time of nano micell production by  $^1\text{H}$  NMR of the solution of the micell type gold particles produced in the beta-mercaptopropionic acid solution of concentration  $10^{-3}$  mol/l which is a peak based on the stainless steel of a vacuum chamber, The spectrum is shown in drawing 6. To the spectrum (A) of only beta-mercaptopropionic acid, micell type gold particles have caused the chemical shift, as (B) shows, and it is shown that the sulfhydryl group of golden particles and a thiol has joined together.

[0017]

[Effect of the Invention]In this invention, the chain which becomes the surface of metal particles from an organic matter was made to adsorb, and metal particles were made into micell type metal particles.

Therefore, metal particles can give the characteristic based on the characteristic of the chain to which it stuck.

Since the characteristics to a fluid, such as solubility, can be given to metal particles, it becomes possible to apply metal particles by applying the fluid which dissolved or distributed

micell type metal particles.

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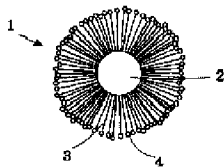
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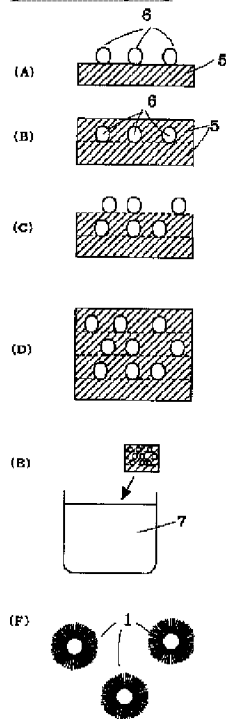
**DRAWINGS**


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[Drawing 1]

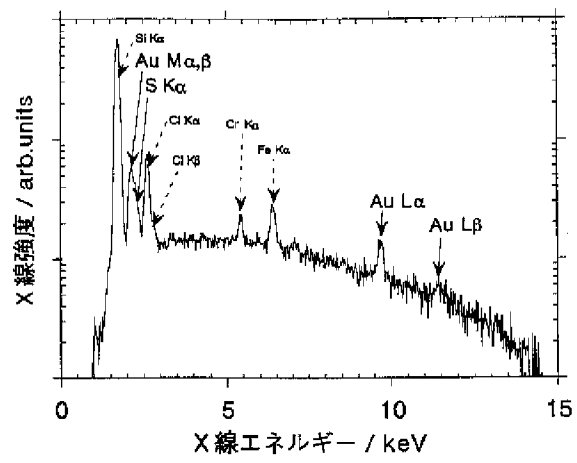


[Drawing 2]

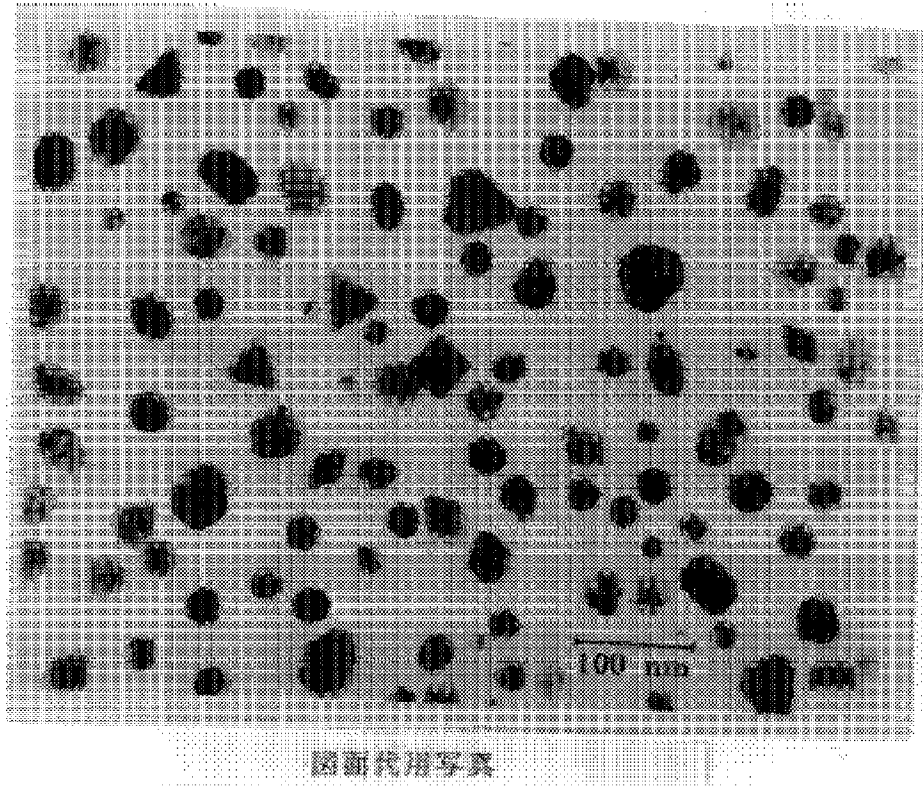


[Drawing 5]

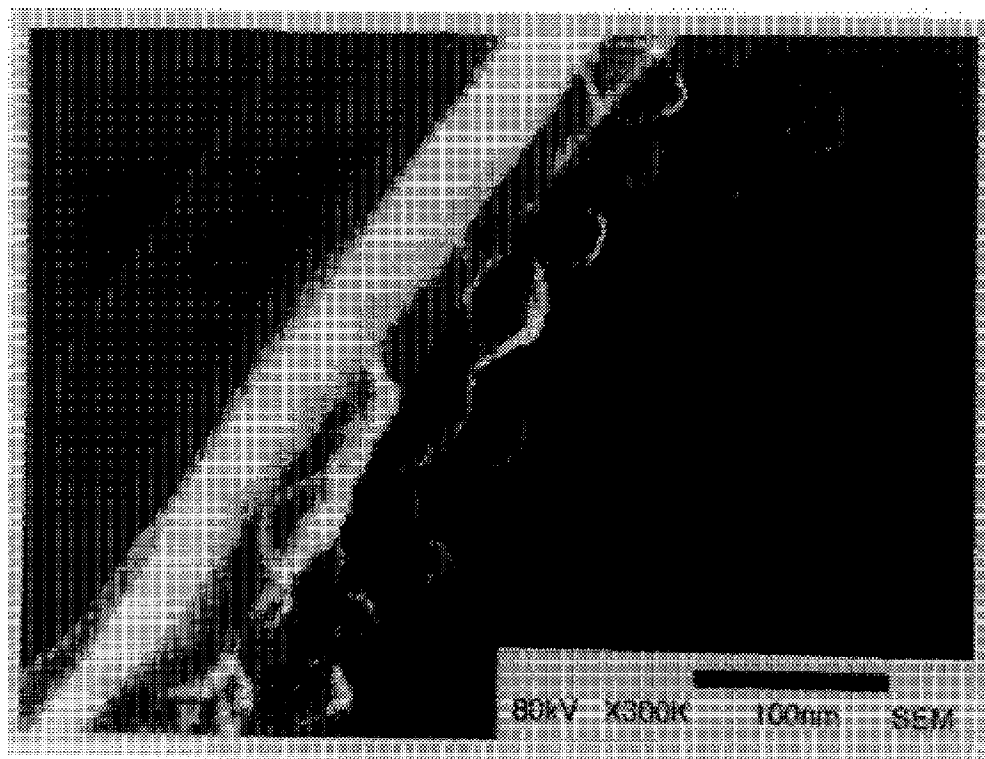




[Drawing 3]

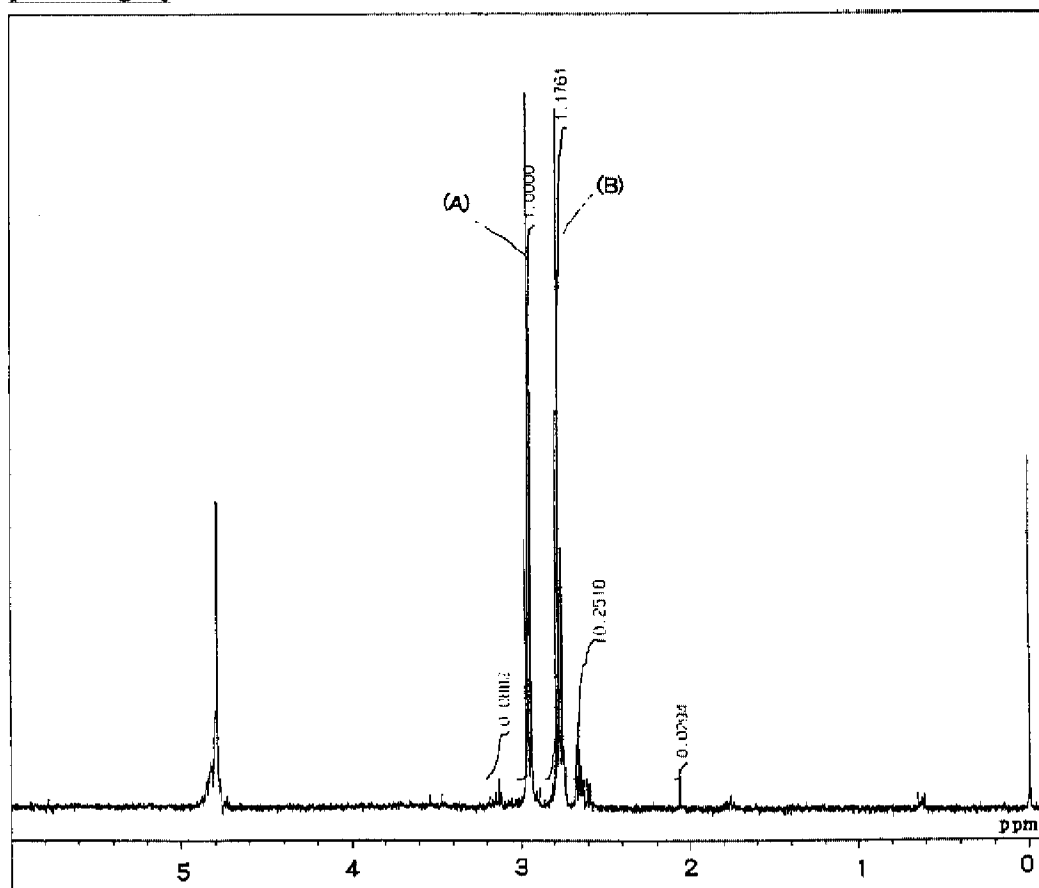


[Drawing 4]



図面代用写真

[Drawing 6]



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